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Chemically synthesized one-dimensional zinc oxide nanorods for ethanol sensing

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ABSTRACT

One-dimensional (1D), single-phase (0 0 2) crystalline zinc oxide (ZnO) nanorod (NR) based conductometric sensors have been developed and investigated toward ethanol (C_2H_5OH) vapor. The ZnO NRs were chemically deposited onto conductometric transducer of alumina substrates employing a simple hydrothermal method. To facilitate the nucleation of ZnO NRs for oriented growth from the substrate, a seed layer of ZnO nanoparticles was pre-deposited employing filtered cathodic vacuum arc (FCVA) deposition technique onto the substrate containing pre-patterned interdigital electrodes (IDTs). Microcharacterization studies revealed that the NRs have a single crystal 1D structure with an average diameter of 30–50 nm. The developed sensors were exposed toward ethanol of different concentrations at temperature up to 330 °C. An optimum sensor operational temperature was found between 280 and 310 °C. At this temperature range, high sensitivity, fast response and fast recovery in conjunction with a stable baseline occur. The long-term stability test of the developed sensors confirmed that they are highly stable with only less than 3% variation of the dynamic performances (baseline resistance, sensitivity, response and recovery time).

1. Introduction

Ethanol (C_2H_5OH) is highly flammable both as vapor and as liquid and has a wide range of applications in industry. It is used as feedstock, disinfectant, solvent, in food components, and as alternative fuel [1,2]. Because of its numerous applications, there is a need for the development of highly sensitive, selective, robust, and inexpensive ethanol sensors. Numerous types of ethanol sensors based on surface and bulk acoustic wave (SAW and BAW), optical, and conductometric transducers have been developed [3–6]. However, due to their small dimensions, low cost, and high compatibility with standard micro-fabrication techniques [3,7,8], conductometric sensors based on semi-conductive metal oxide thin films are the most promising. Recent focus addresses the application of nanostructured materials to enhance the performance of the sensors.

Interactions of gas molecules with the surface of the semiconductors lead to changes in the electrical conductivity [9–11]. The gas sensing mechanism involves chemisorption of oxygen on the oxide surface which is followed by a charge transfer during the reaction of chemisorbed oxygen with the analyte gas [9]. An extensive numerical modeling on this is given in Ref. [12]. Recently, utilization of one dimensional (1D) metal oxide nanostructured materials in the forms of nanobelts and nanorods as gas sensing elements have gained great attention in the scientific community [13]. The use of nanobelts, nanorods, and various other nanostructures offers higher surface to volume ratio compared to polycrystalline and bulk metal oxides. Furthermore, it has been reported that the performance of solid-state gas sensors improves with a reduction in the oxide particle size [14]. It promotes rapid interaction between the gaseous molecules and the oxide particles, as the entire thickness of the sensitive layer can be affected by the redox reaction during the process. As a result, the dynamic performance of a gas sensor using a one-dimensional (1D) single crystalline nanostructure will improve significantly compared to polycrystalline and bulk metal oxides [15]. In recent years, many methods have been reported in the fabrication of 1D nanostructures [13–16].

Among the semiconductor metal oxides, zinc oxide (ZnO) is the most widely applied gas sensing material due to its high mobility of conduction electrons and good chemical and thermal stability [16]. Various forms of ZnO such as single nanowire, thick films, thin films, and heterojunctions are used for gas sensing [17–20]. Numerous sensors for gases/vapors such as H_2, NO_2, methanol, C_2H_5OH, H_2S, CH_4, and CO have been reported [6,16,21–25]. 1D ZnO nanorods (NRs) based thin film gas sensors have been studied by a number of researchers who reported that enhanced performance was achieved compared to their bulk and coarse micro-grained ZnO

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sensor counterparts [13,26,27]. 1D ZnO NRs have been obtained by numerous methods, including RF sputtering [28], chemical and physical vapor deposition [29,30], metal organic chemical vapor deposition (MOCVD) [31], pulsed laser deposition [26], as well as electrochemical [27] or hydrothermal processes [7,32]. In the hydrothermal method, a ZnO seed layer was pre-deposited for the growth of well-aligned NRs. Several studies report on seed layers prepared by RF sputtering, spray pyrolysis, pulse laser, dip coating, or spin coating [33–36]. However, seed layers deposited using these methods have more than one crystallographic phases and are not uniform. As a result, hydrothermally grown NRs from these seed layers have multiple crystallographic phases. The presence of single crystallographic phase on the seed layer is required for the growth of 1D ZnO nanorods during hydrothermal process. To the best of authors' knowledge, this is the first report to grow 1D ZnO nanorods employing filtered cathodic vacuum arc (FCVA) deposited ZnO seed layer with single crystallographic phase (0 0 2) using a hydrothermal method. The advantage of FCVA deposition technique is that the energy of the depositing species can be controlled using substrate bias. In this work, by tuning the substrate bias voltage we have successfully grown ZnO seed layer with single crystallographic phase. The response of the ZnO NRs-based sensor toward various concentrations of ethanol are reported. The performance of the sensor was investigated at different operating temperatures ranging from 200 to 330 °C.

2. Experimental

The sensor platform used in this work was fabricated using thick-film technology. On the top side of a 96% alumina substrate, IDTs with 30 μm line/space were deposited. Since such fine-line printing is not possible using standard thick-film technique, the IDT electrodes were prepared by laser patterning of fired gold film. Applications of frequency-tripled Nd:YAG laser with wavelength of 355 nm and beam diameter of 20 μm allows to obtain clean and precise cut as described in [37]. The whole structure had dimensions of 9.75 mm × 3.5 mm. Prior to film deposition, the transducers were cleaned in an ultrasonic bath with acetone then ethanol, and dried with N_2 at room temperature.

A double-bend FCVA deposition system with a 99.9% pure zinc (Zn) cathode at an arc current of 40 A and a base pressure less than 2×10^{-5} Torr, was used to deposit ZnO seed layers onto the transducer. The cathodic arc deposited samples were mounted on a metallic substrate holder which was supported on a variable temperature heater capable of maintaining a temperature of up to 600 °C. A stainless steel mesh was placed between the source and the substrate and connected to a regulated DC power supply, allowing the control of the mesh bias voltage. The mesh consisted of 0.45 mm diameter steel wires with open areas of 0.8 mm × 0.8 mm. It was placed 11 mm in front of the substrate. The plasma flow direction was perpendicular to mesh and substrate. In FCVA, the depositing flux is almost 100% ionized so that the energy of the depositing species can be controlled using a substrate bias. In this experiment, mesh bias was used instead of direct substrate bias as alumina is insulating. During deposition, the oxygen partial pressure was maintained constant at 1.15 mTorr with a substrate temperature of 200 °C and a mesh bias voltage of −100 V. The thickness of the deposited films was measured using a Tencor P-16 profilometer and found to be 20 nm (approximately). The ZnO seed layer serves as a nucleation site during the chemical synthesis.

During the chemical synthesis stage, the transducers with the FCVA deposited ZnO seed layer were placed inside a custom made reaction vessel. The vessel was filled with an equimolar aqueous solution of zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] and hexamethylenetetramine or HMT ($C_6H_{12}N_4$), diluted in 200 ml of de-ionized water. It was prepared based on a modified method first described by Vayssieres [38]. The growth temperature was set at 80 °C and the deposition time was 16 h. Following this, the coated transducers were removed and washed with DI water to eliminate any residual zinc salts and subsequently dried in a stream of N_2 prior to microstructural and electrical characterization. The deposition sequence of ZnO NRs is schematically shown in Fig. 1.

Surface morphology of ZnO nanostructures was investigated using a FEI Nova Nano scanning electron microscope (SEM). The chemical composition and crystallographic phase of the ZnO thin films (both seed layer and NRs) deposited on the substrate was determined by X-ray diffraction (XRD). XRD was carried out using a Bruker D8 Discover micro-diffractometer fitted with a GADDS (General Area Detector Diffraction System) with a potential of 40 kV and a current of 40 mA, and filtered with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes). Data was collected at room temperature using Cu Kα radiation (λ = 1.54178 Å).

In electrical characterization, the sensor was mounted in a gas chamber and exposed to different concentrations of ethanol balanced in synthetic air. A multimeter (Keithley 2001) was used to measure changes in conductivity. A data acquisition computer with Labview software (National Instrument) was used to collect the data in real time. A heater (250 Ω, 10 W) was mounted on the backside of the sensor. A DC power supply was connected to the heater to control the operational temperature. A thermocouple was placed onto the top of the sensor's surface for real time temperature monitoring. By a computer-controlled mass flow controller (MFC) system, the ethanol concentration (balanced in synthetic air) was adjusted. The experimental gas testing setup is shown in Fig. 2. The gas mixture was delivered at a constant rate of 200 sccm. The gas exposure time was fixed for each pulse of ethanol vapor and the cell was purged with synthetic air between each pulse allowing the sensor response to recover to initial conditions. The sensor was exposed toward ethanol concentrations of 12.5, 31.25, 62.5, 187.5, 250, 375 and 500 ppm at operating temperatures between room temperature to 330 °C.

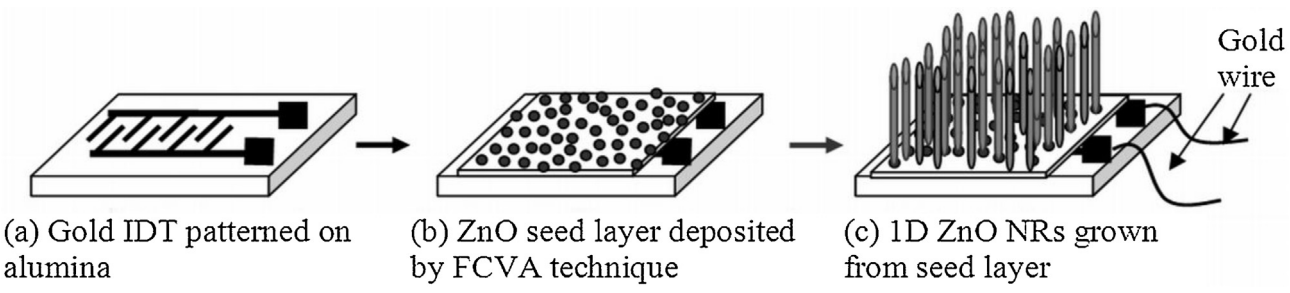

Fig. 1. A schematic representation of the deposition method configuration of ZnO NRs.